



High Temperature Ferroelectrics for Actuators: Recent Developments and Challenges

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Venus

- Development of Earth-like planets in our solar system and elsewhere.
- Pathways toward habitable environments.
- Determine planet evolution: The nature, geochemical composition, surface and atmosphere interaction and the role of impacting objects.
- Venus is a planet very similar to Earth in mass, size and bulk density, but very different in surface environment and general geology.
- The Venera and Vega lander missions were accomplishments, but their chemical analyses did not permit detailed confident interpretation by the standards of terrestrial rock analyses.
- The harsh Venus environment caused short mission durations under two hours.

Surface Temperature:

467 °C

Hotter than Mercury due to atmosphere

96.5% carbon dioxide (CO₂)

3.5% nitrogen (N₂)

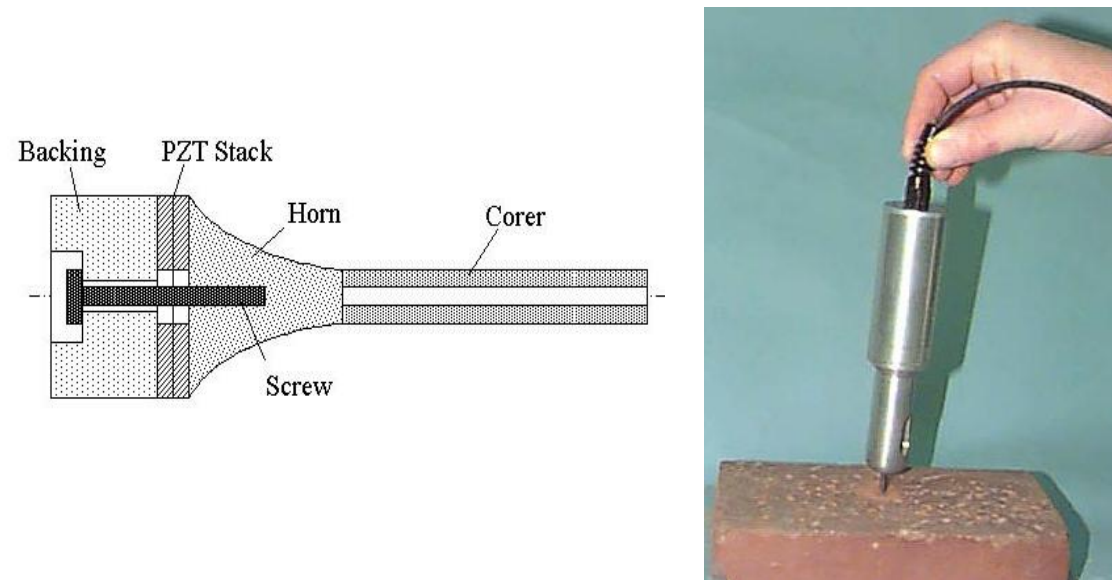
Surface Pressure

92 bars

High radiation and chemical/physical corrosion

Ultrasonic drilling

- Future NASA missions, New Frontier (Venus In-Situ Surface Explorer) and Flagship (e.g., Venus Surface Explorer and Venus Sample Return), will require advanced surface drilling technology to extract cores from the subsurface.
- Ultrasonic drills driven by piezoelectric motors offer significant advantages over rotary electric motors in terms weight, volume, and power requirement.
- Technology developed by Jet Propulsion Laboratory and Cybersonics.



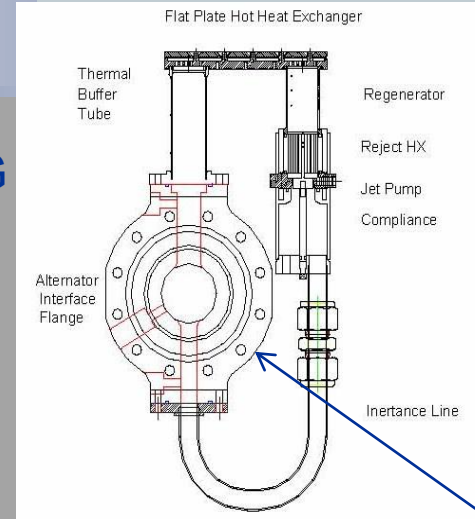
Y. Bar-Cohen, Z. Chang, S. Sherrit, M. Badescu and X. Bao, Proceedings of SPIE: Smart Structures and Materials, **5762**, 152-159, (2005).

The ultrasonic drill design is compact, low mass of 450 grams and low power consumption of 5W. Presently, ultrasonic drill technology does not exist for harsh environments due to low operational temperature of the piezoelectric materials.

Piezoelectric actuators are smaller, lighter, cheaper and outperform magnetostrictive actuators at high frequencies

Motivation

- Stirling heat engine technology to replace RTG
- Increase conversion efficiency, reduce launch mass (specific power $> 10 \text{ W/kg}$) and reduce cost.
- Reduces the Pu238 mass for safety cost.
- Several technical challenges: vibrations, electromagnetic interference and reliability/life due to piston motion.



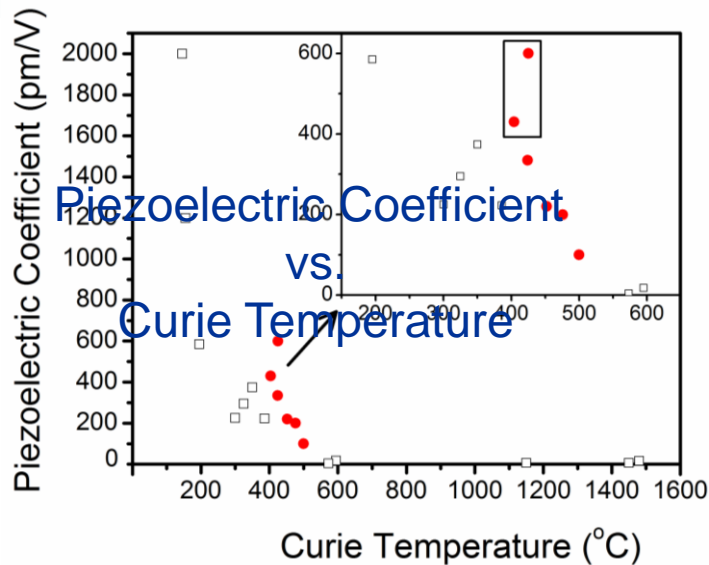
Piezoelectric
replaces
alternator

- Piezoelectric technology eliminates electromagnetic interference, enhances reliability/life by eliminating motion, reduces vibration caused by piston motion and reduces mass by eliminating magnets and coils required for power generation.
- Stirling engines have conversion efficiency on the order of 20-30%, linear alternators operate with $>90\%$ efficiency
- Achieve 10-100 watt generator using piezoelectric technology.

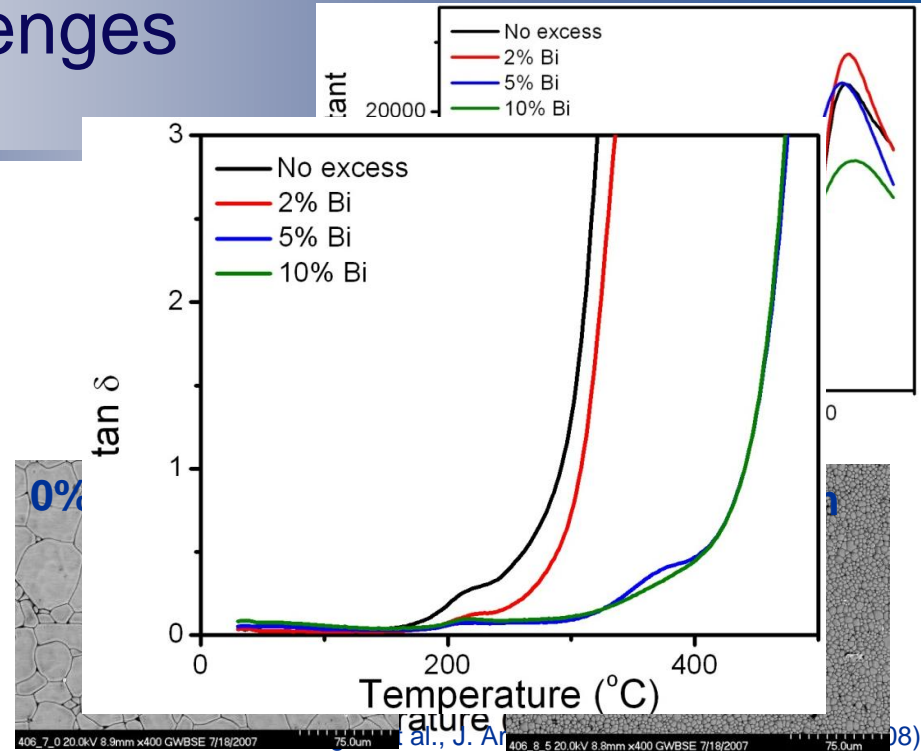
Baseline Review

- Nine proposed missions to the surface of Venus launching between 2016-2040
- No other technology capable of supporting long-lived surface operations

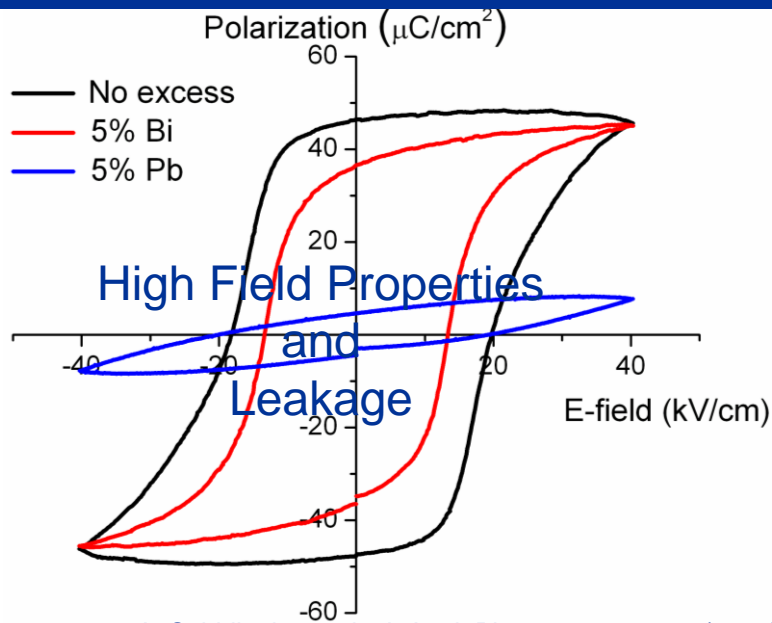
Challenges



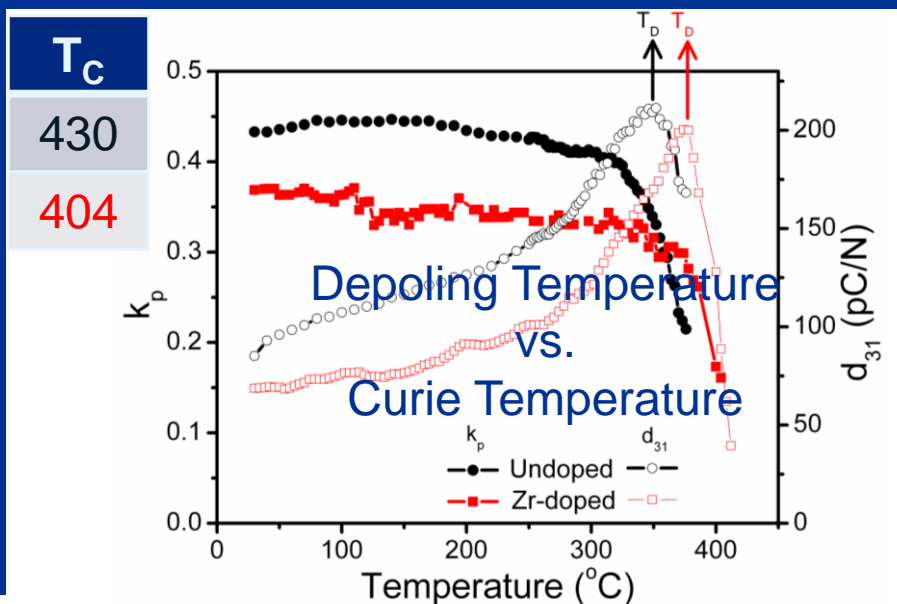
A. Sehirlioglu, et al., J. Appl. Phys. **106**, 014102 (2009).



A. Sehirlioglu, et al., J. Appl. Phys. **106**, 014102 (2009).



A. Sehirlioglu, et al., J. Appl. Phys. **106**, 014102 (2009).



A. Sehirlioglu, et al., J. Am. Ceram Soc., **93** [6], 1718 (2010).

Thermal Depoling Temperature

Thermally activated randomization of domains in ferroelectrics resulting in decreasing net polarization and piezoelectricity with or without a FE-FE or $T > T_f$ phase transformation.

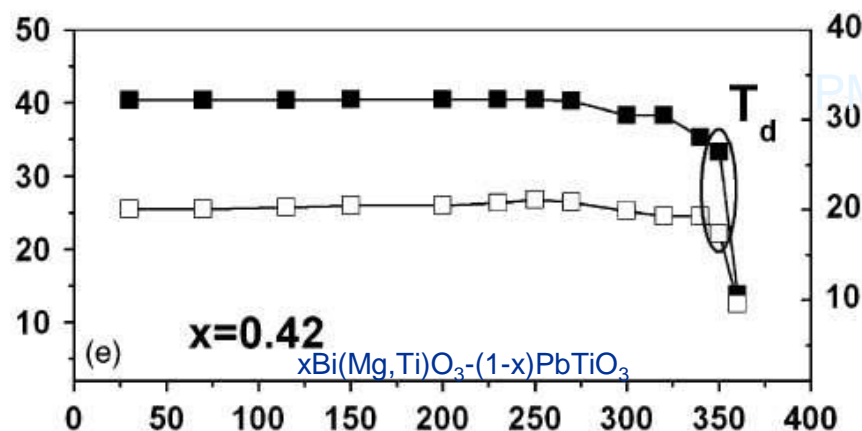
Weakening of bonds between A-site cations and oxygen atoms.

How to define depolarization: E.M. Anton, W. Jo, D. Damjanovic, and J. Rödel, J.Appl.Phys. **110**, 094108 (2011)

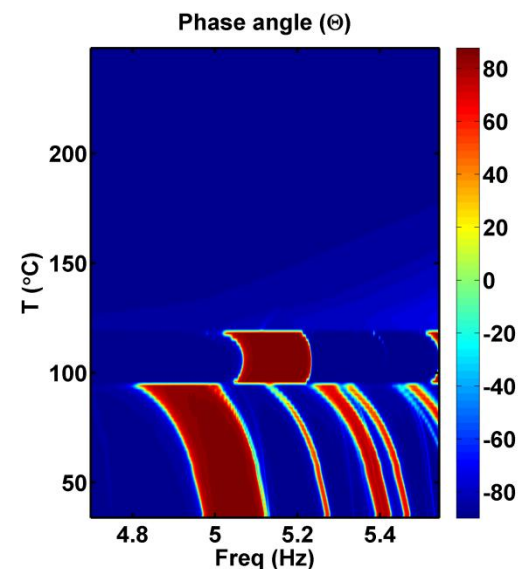
T_d = the temperature of the steepest decrease of remanent polarization.

- 1- Thermally stimulated depolarization current
- 2- Dielectric constant / $\tan \delta$ characteristics as a function of temperature
- 3- Resonance peaks and electromechanical coupling coefficients.
- 4- Annealing and room temperature d_{33}
- 5- In-situ XRD
- 6- In situ temperature-dependent piezoelectric coefficient d_{33}

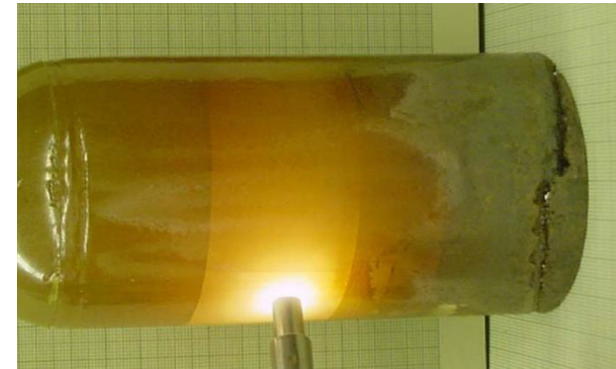
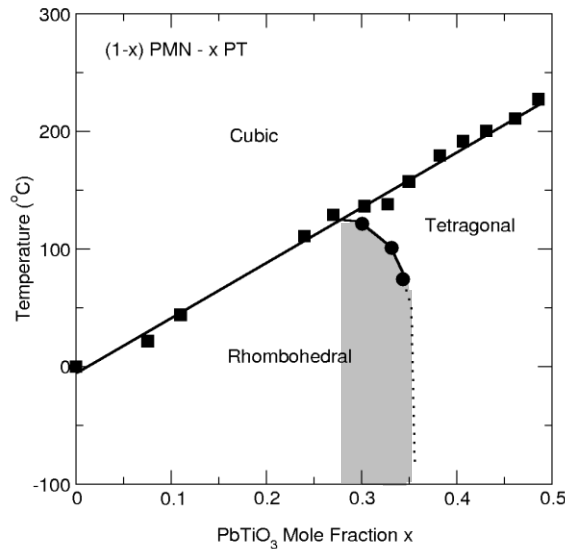
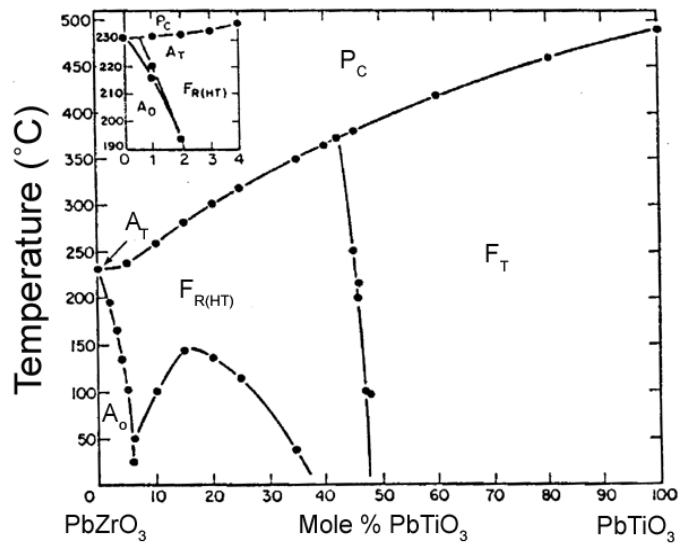
FE-FE does not always lead to depolarization



Qiang Zhang, Zhenrong Li, w Fei Li, Zhuo Xu, and Xi Yao, J. Am. Ceram. Soc., 93 [10] 3330–3334 (2010)



Piezoelectric Ceramics

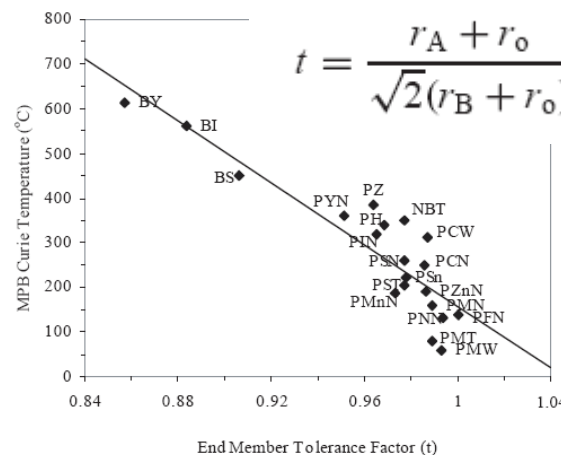
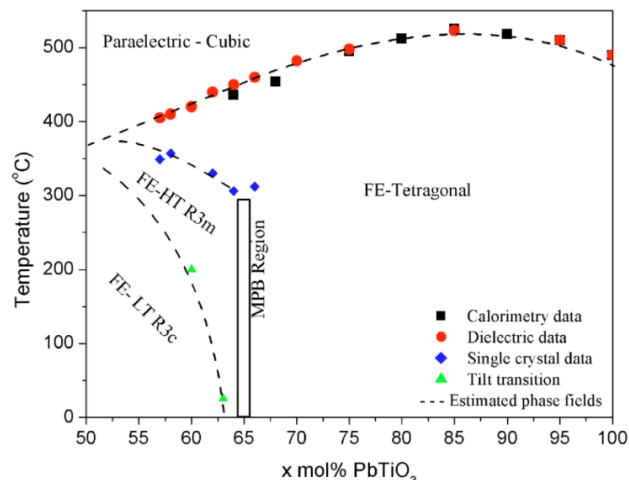


H.C. Materials Corp.

A. Sehirlioglu, P.D. Han, and D.A. Payne, J. Appl. Phys. **99**, 064101 (2006).

B. Jaffe, W. R. Cook and H. Jaffe, Piezoelectric Ceramics, Academic Press, New York, 1971.

Shrout T., Zung P. C., Namchul K., Markgraf S. Ferroelectrics Letters **12**: 63-69, 1990.



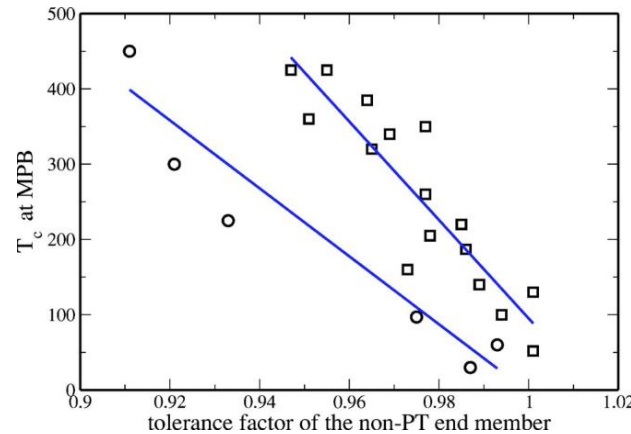
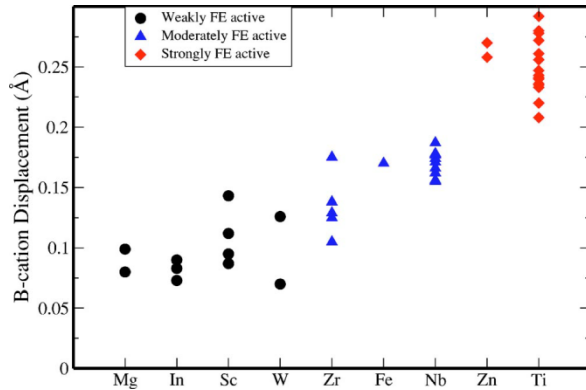
- Tri→M→PC→R→T
- Hybridization of Bi-6p and O-2p orbitals drive the FE instabilities.
- Strong Bi- O covalency favoring FE and high Tc.
- Competition between presence of Bi and decreasing t for FE activity, and random field effects

R.E. Eitel, S.J. Zhang, T.R. Shrout, C.A. Randall, and I. Levin, J. Appl. Phys., **96** [5] 2828-31 (2004).

R.E. Eitel, C.A. Randall, T.R. Shrout, P.W. Rehrig, W. Hackenberger and S.E. Park, Jpn. J. Appl. Phys., **40** Pt.1 [10] 5999 (2001).

Inaguma et al., J. Appl. Phys. **95**, 231 (2004)

Guidelines

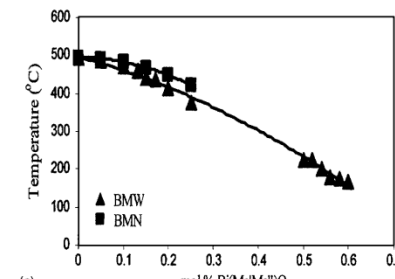
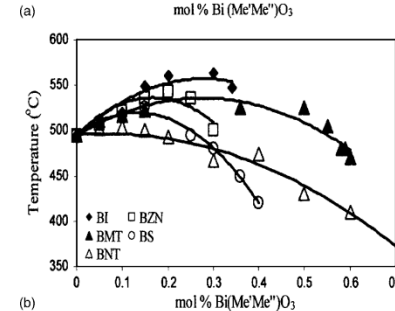
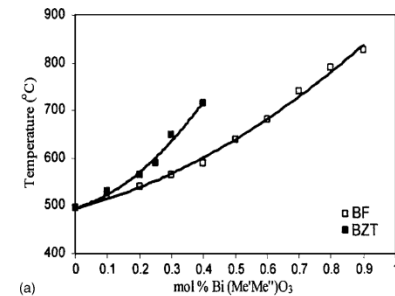


I. Grinberg, M. Suchomel, P. Davies, and A. Rappe, J. Appl. Phys., **98** 094111, (2005).

case 1: $b > 0$ and $c > 0$,
 case 2: $b > 0$, $c < 0$, and $|2c| > b$,
 case 3: $b < 0$ and $c < 0$,

$$T_c(x) = a + bx + cx^2$$

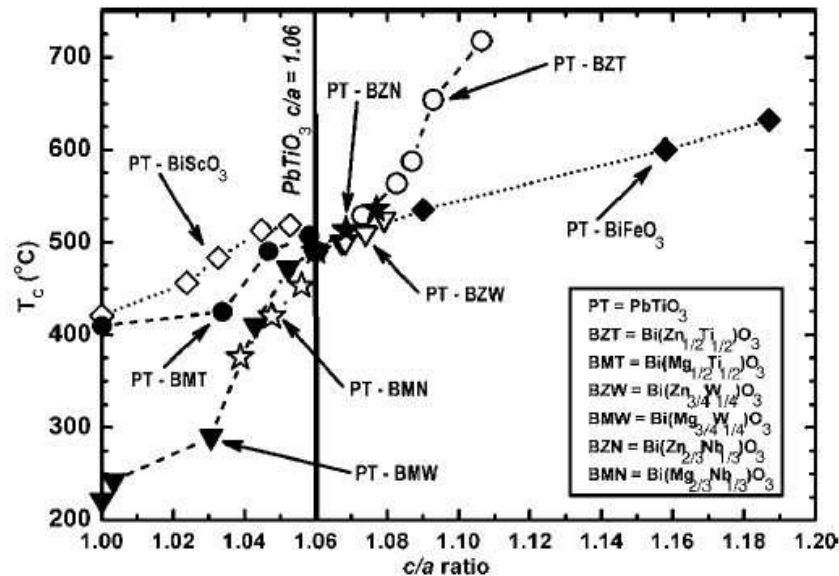
- A-site distortion magnitude depends on the B-site cation
- In T phase – larger cations forming (001) face, (i) smaller displacement, (ii) tilt in the distortion direction.
- Larger B cations will shift the $x(\text{MPB})$ to higher PT content



C. J. Stringer, T. R. Shrout, C. A. Randall, and I. M. Reaney, Journal of Applied Physics **99**, 024106 (2006);

- Additional requirement for t-Tc trend: Enhancement of Tc in tetragonal phase (Case II)
- Spread of tolerance factor Δt : Difference between max and min permissible t in a solid solution. $V, \text{Mn}, \text{Al}, \text{Ni}$
- Variance of B-site ionic radius (σ^2).
- Effectively, the largest Δt and σ^2 values give the greatest enhancement in transition temperature.
- Random strain fields

High T_c with high tetragonality = problem



Stein, Suchomel, and Davies Appl. Phys. Lett. **89**, 132907 2006

$xBiFeO_3$ -(1-x) $PbTiO_3$: R3c, T_c = 836°C,

- MPB: $x=0.66-0.73$
- c/a near MPB: 1.187 (1.06 for PT)
- Possible intermediate phase at MPB
- Fragile: large c/a and NTEC

Properties:

- Highly conductive
- Difficult to pole both due to tetragonality and conductivity (ferroelastic measurements show unstable domains)
- Thermal hysteresis
- Adding $BaTiO_3$ improves resistivity at the cost of T_c but the dielectric losses remain high.
- Attempts to decrease conductivity, decreased T_c

Kouna Njiwa et al., J. Am. Ceram. Soc., 89 [5] 1761 (2006)

$xBi(Zn,Ti)O_3$ -(1-x) $PbTiO_3 \rightarrow$ similar problems to BF-PT. Zn, Ti, and Fe are all FE-active, stronger coupling between A- and B-site distortions.

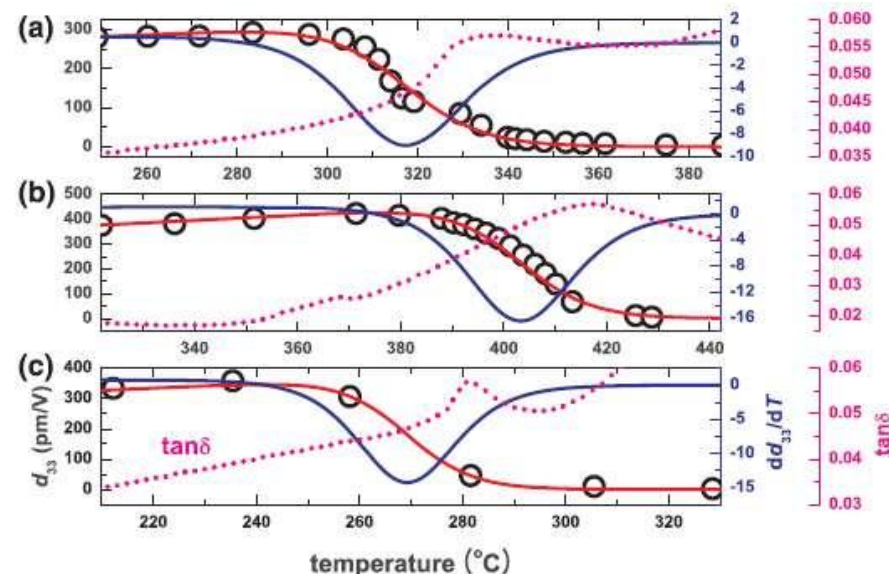
vs. $xBi(Mg,Ti)O_3$ -(1-x) $PbTiO_3$: Mg^{2+} :72pm, Zn^{2+} :74pm \rightarrow importance of off-centering
MPB $x=0.37$, higher T_c than BS, lower d_{33}

vs. $xBi(Zn,Zr)O_3$ -(1-x) $PbTiO_3$: Zr^{4+} :72pm, Ti^{2+} :60.5pm \rightarrow limited displacement of Zr
limited solubility, MPB cannot be processed.

Case II materials

- Necessary to get high T_c at the MPB
- $x\text{Bi}(\text{Mg},\text{Ti})\text{O}_3-(1-x)\text{PbTiO}_3$ $T_c > 400^\circ\text{C}$, $d_{33} > 200\text{pm/V}$
 - R3c-P4mm core shell structure at MPB with R core and T shell, with frozen in polarization state (no frequency dispersion).
 - Poling can change the local symmetry
Randall et al., Journal of Applied Physics **95**, 3633 (2004)
- $x\text{Bi}(\text{Ni},\text{Ti})\text{O}_3-(1-x)\text{PbTiO}_3$
 - High conductivity and dielectric losses
Choi et al., J. Appl. Phys. **98**, 034108 (2005).
- BMT metastable, high pressure synthesis, O, AFE, with strong driving force for ordering
Suewattana et al. Phys. Rev B **86**, 064105 (2012)
- At 325°C pseudo-cubic peak appears – so there might be a phase coexistence range (similar to BF-PT, BS-PT)
Chen et al., Journal of Applied Physics **106**, 034109 (2009)
- T_d lower for d_{33} than $\tan \delta$, d_{33} reflects the temperature where a structural instability starts. BMT-PT, BS-PT, BF-PT-La

Leist et al., J. Am. Ceram. Soc., 95 [2] 711–715 (2012)



Leist et al., J. Am. Ceram. Soc., 95 [2] 711–715 (2012)

Reports on mixed phases as a function of Temp:

- T+C in BZT-PT and BS-PT (coexistence range varying from $>100^\circ$ down to 5° with increasing PT content. 111 invariant plane.
- $T1+R \rightarrow T1+T2+R$ for BF-PT

Lalitha et al. J. Am. Ceram. Soc., 95 [8] 2635–2639 (2012)

Kothai et al. J. of Appl. Phys. **113**, 084102 (2013);

Two volatile species = a more complicated world

What we learned from PZT, guides us but not always applicable the same way.

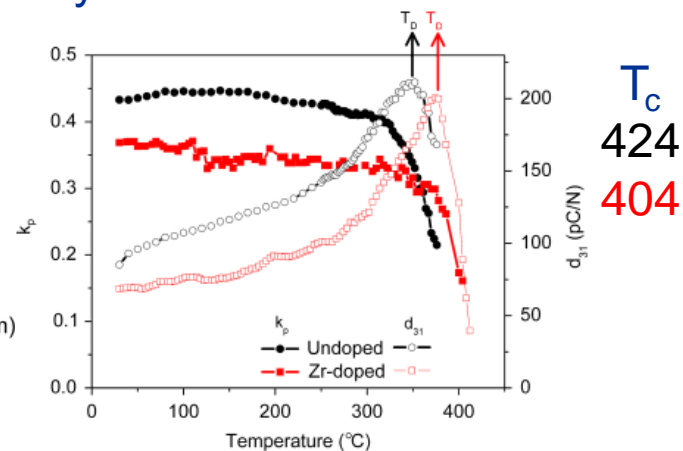
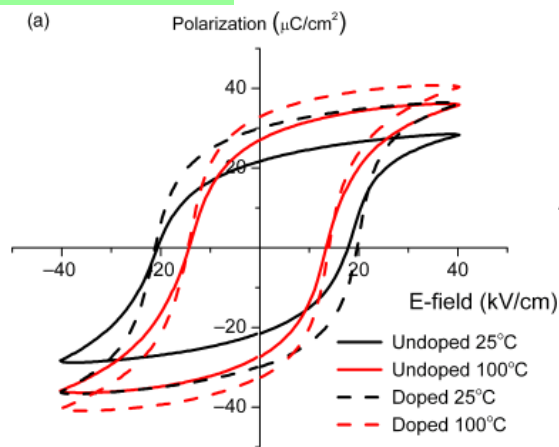
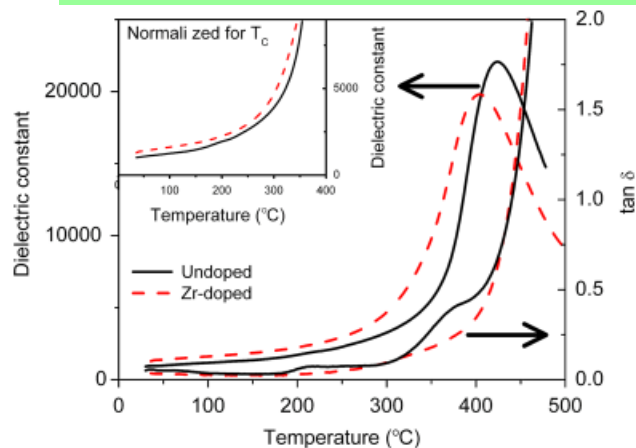
- Effect of dopants are material specific [i.e., Donor doping with volatile species (PZT) vs. non-volatile species (BaTiO_3)]
- La_{Pb} , Nb_{Ti} does not have the same enhancements. Mn is the most successful dopant.
- Zr_{Sc} = not multi-valent, cannot be used in PZT as an aliovalent dopant.

Observations:

- Increased dielectric constant
- Lower temperature dependence of FE properties
- Square hysteresis loops
- Higher symmetry in bipolar measurements

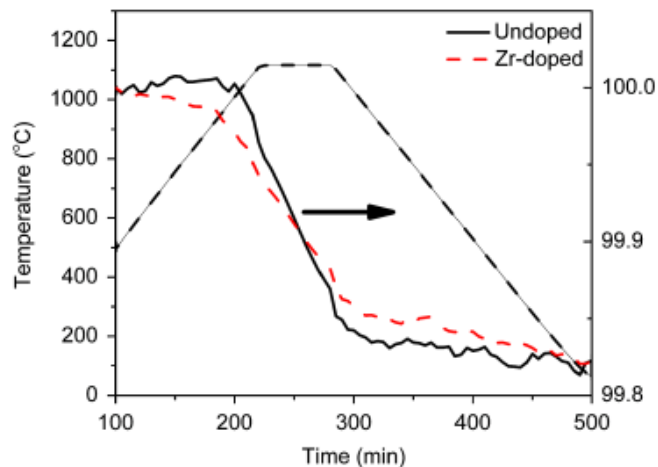
- Decrease in electromechanical coefficients
- Lack of change in E_c

“On the basis of vacancies facilitating domain boundary motion”

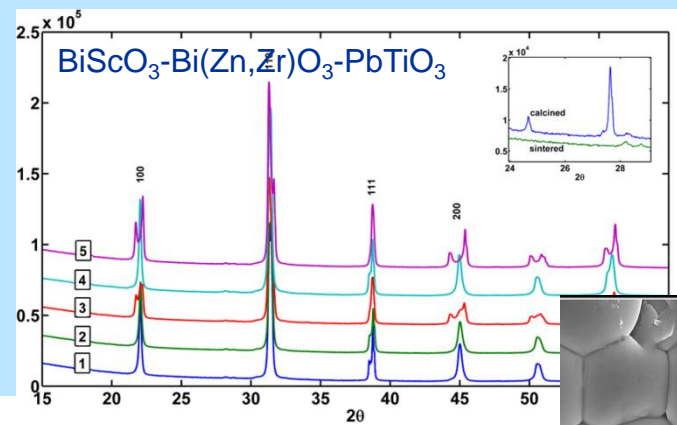


T_c
424
404

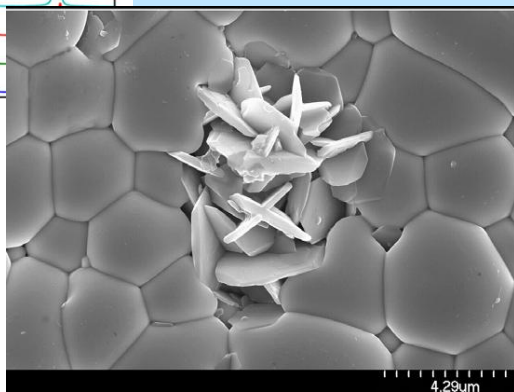
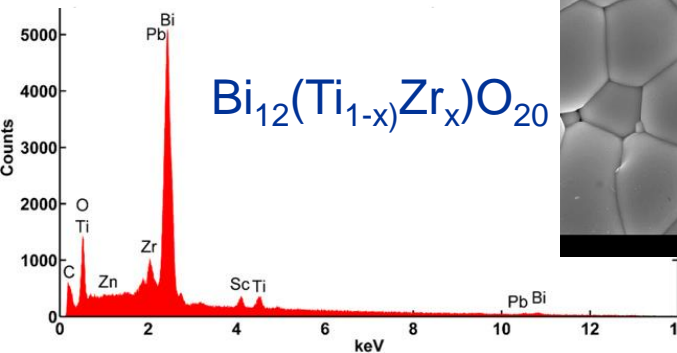
Two volatile species = a more complicated world



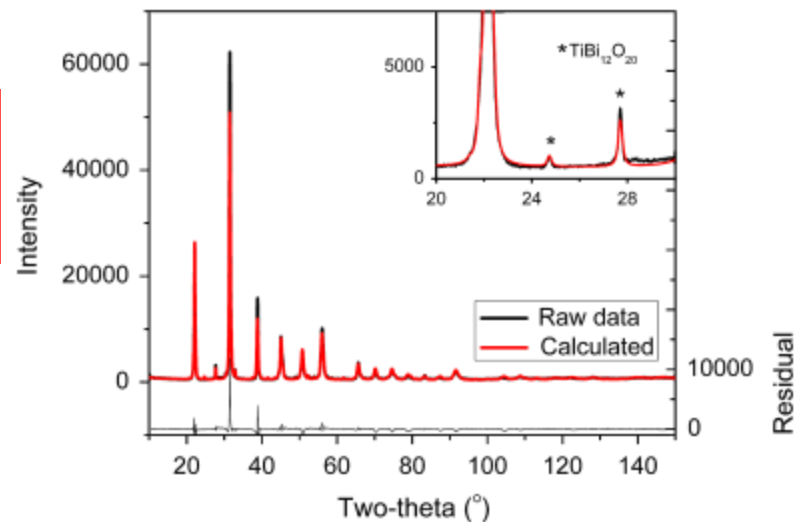
- TGA: Weight change in flowing oxygen/air for both doped and undoped $\approx -0.18\%$.
- During sintering with sacrificial powder:
Undoped: $<2\%$, Doped: $+0.15-0.3\%$.
- Sintering atmosphere: $\approx 90\text{Pb}-10\text{Bi}$



Pb'Bi?



B. Kowalski, et al., J. Amer. Soc. published online (2013).

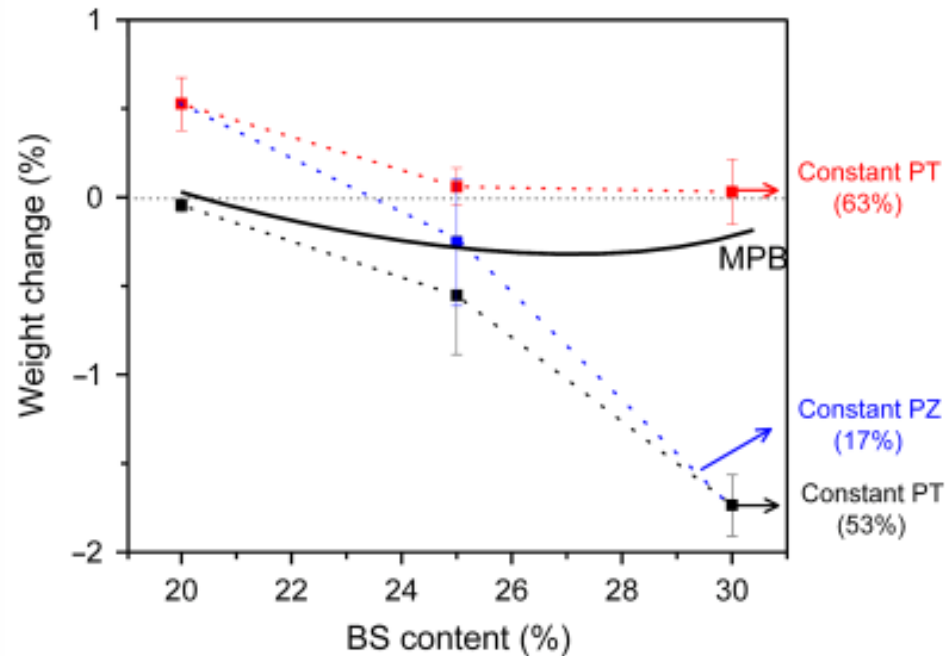
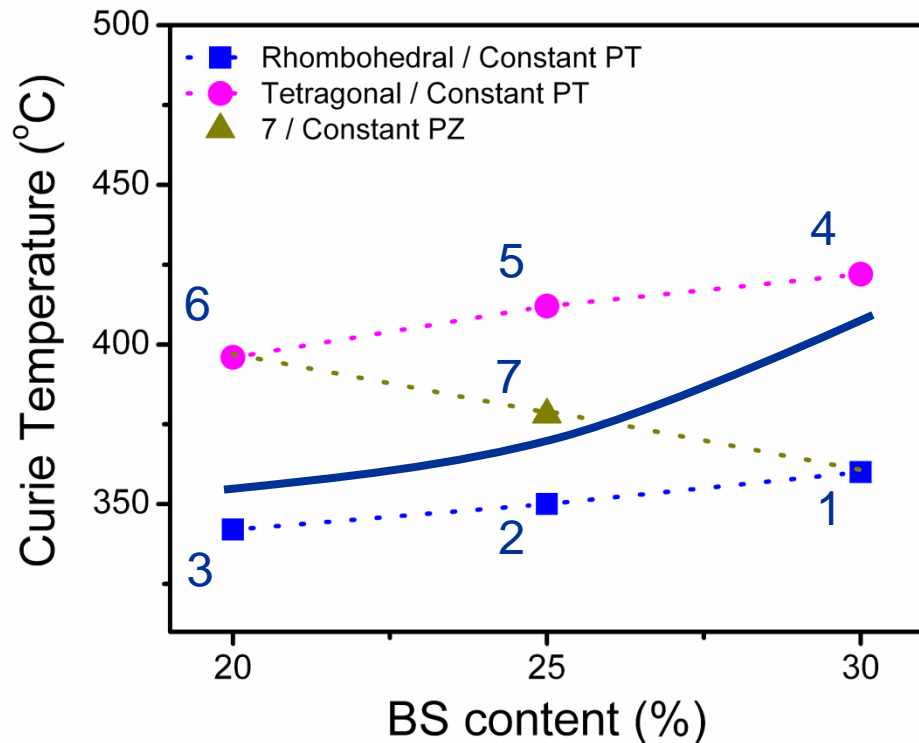
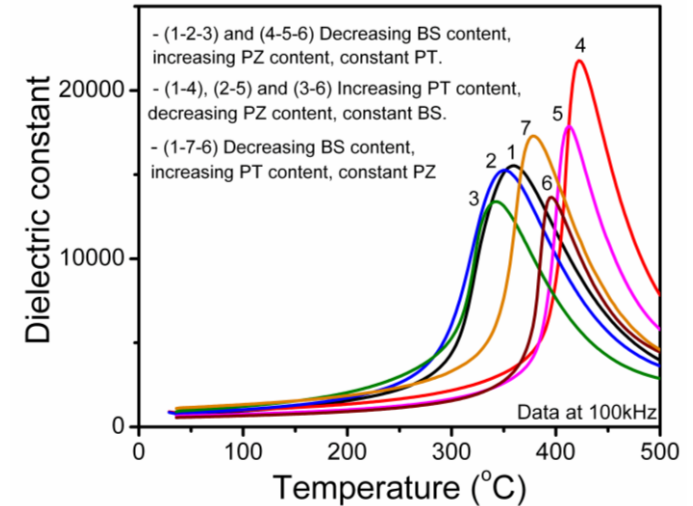
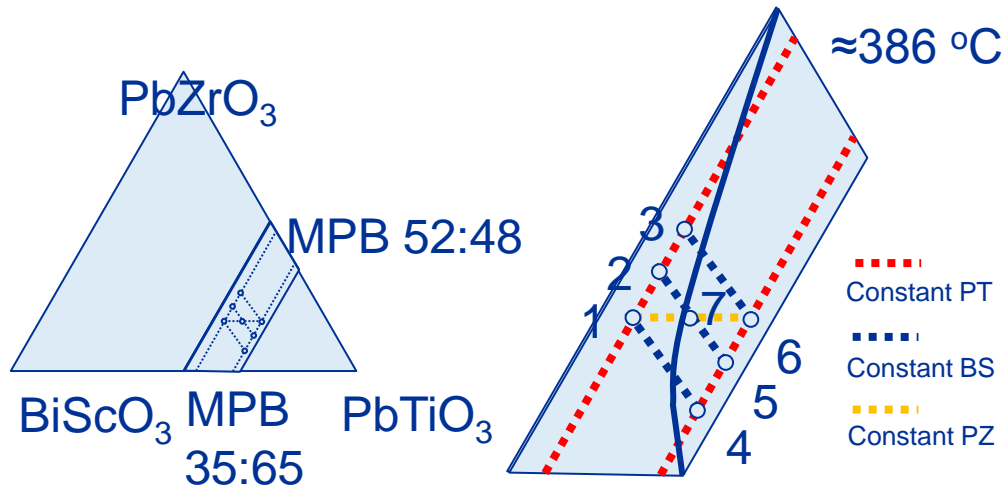


- Bismuth containing second phase

%	R	T
Undoped	60	37
Doped	25	72

A. Sehrioglu, et al., J. Amer. Soc. **93** [6], 1718, 2010

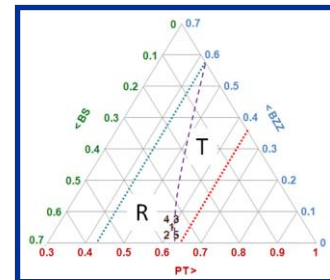
Structure specific behavior?



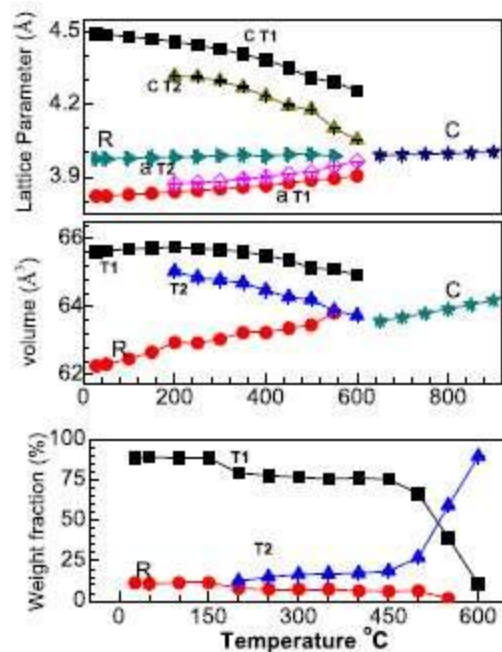
Perovskite but which symmetry?

In BF-PT different ranges have been reported to be MPB (PT = 0.27-0.40 range)

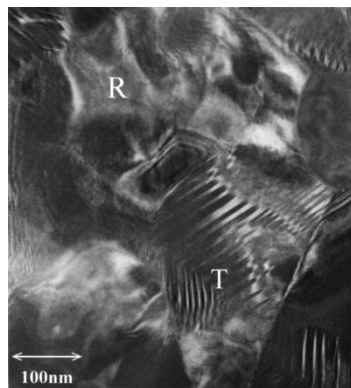
- R and T ratio differences for same composition near MPB.
Not observed away from MPB
- R phase crucial to keep the samples mechanically intact.
- Energy difference between R and T is small near MPB
- Local kinetic factors determine if metastable R will form.
- Samples are not inhomogeneous (microprobe/broadening)



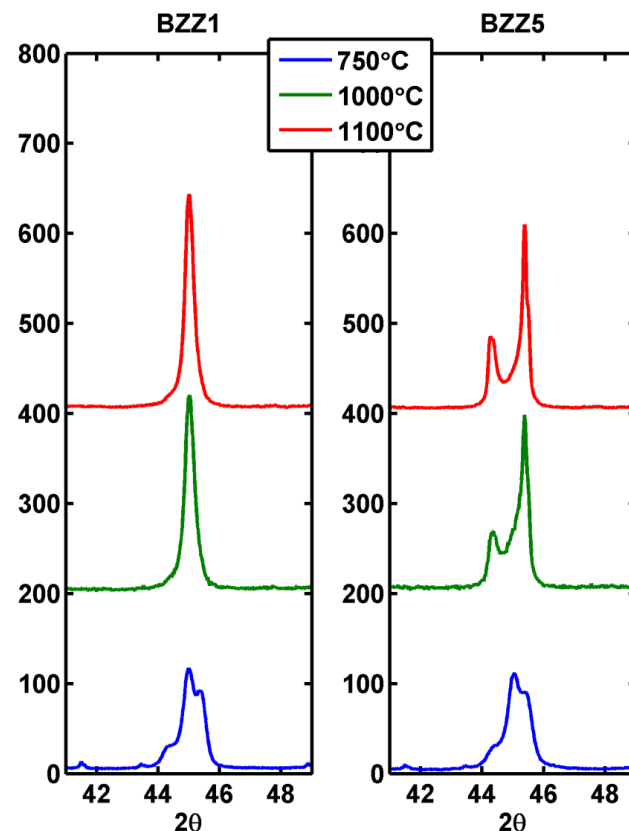
Temperature over time



- T1-T2 difference is the extent of hybridization
- R phase 11% → 7% with temperature. (R3c)
- R+T needs to be shared in the same grain.



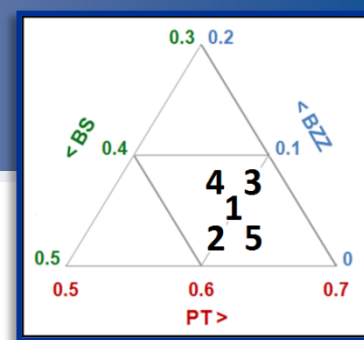
It was claimed to be due to sample prep.



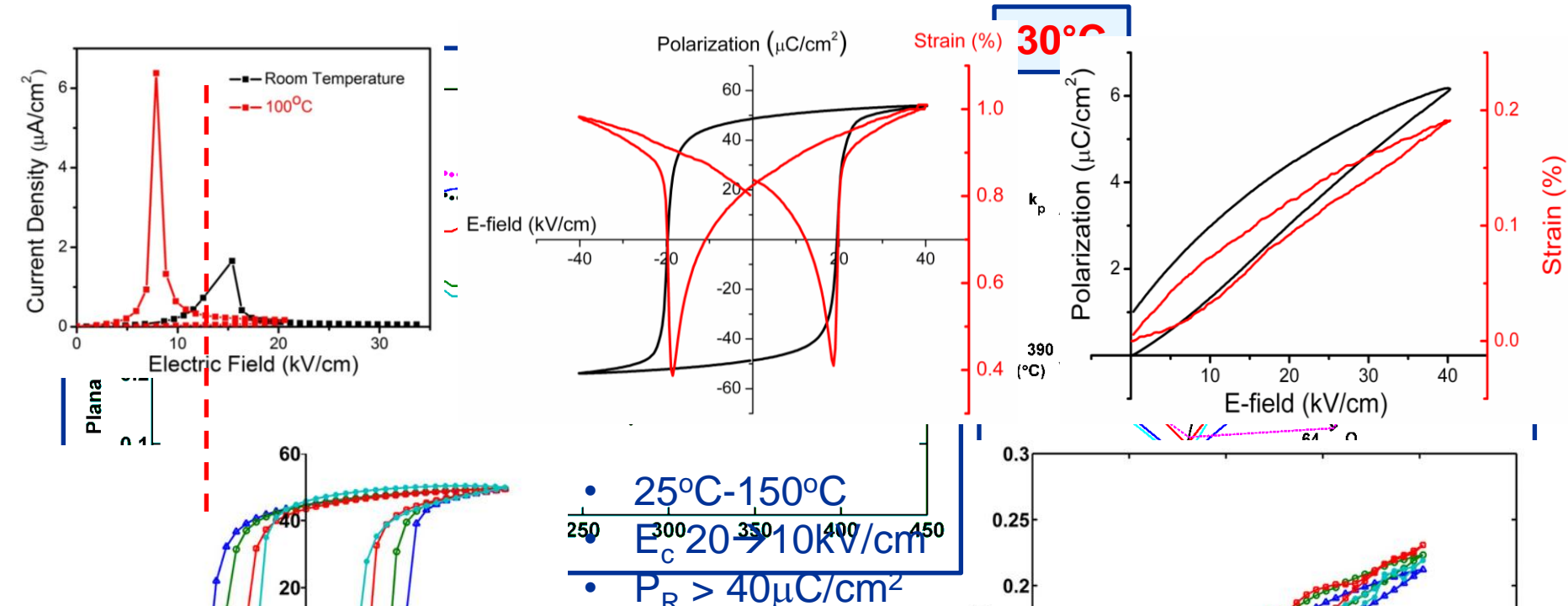
Kothai et al. J. of Appl. Phys. **113**, 084102 (2013)
Bhattacharjee et al. Phys.Rev. B **84**, 104116 (2011).

D. I. Woodward et al., J. Appl. Phys. **94**, 3313 (2003).

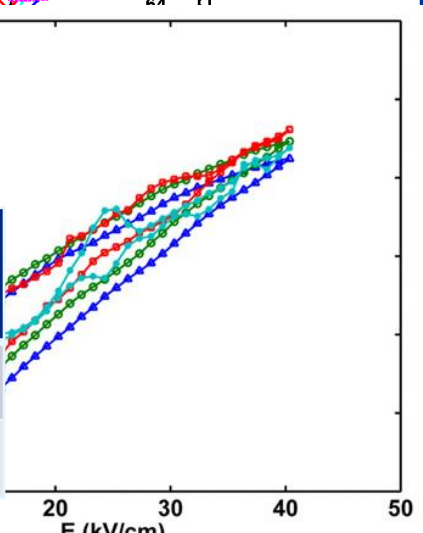
BiScO₃-Bi(Zn,Zr)O₃-PbTiO₃



- Zn and Zr are ferroelectrically more active than Sc
- Average radius of (Zn_{1/2},Zr_{1/2}) (73pm) is close to that of Sc (74.5pm)
- No increase in tetragonality due to existing Bi in the system



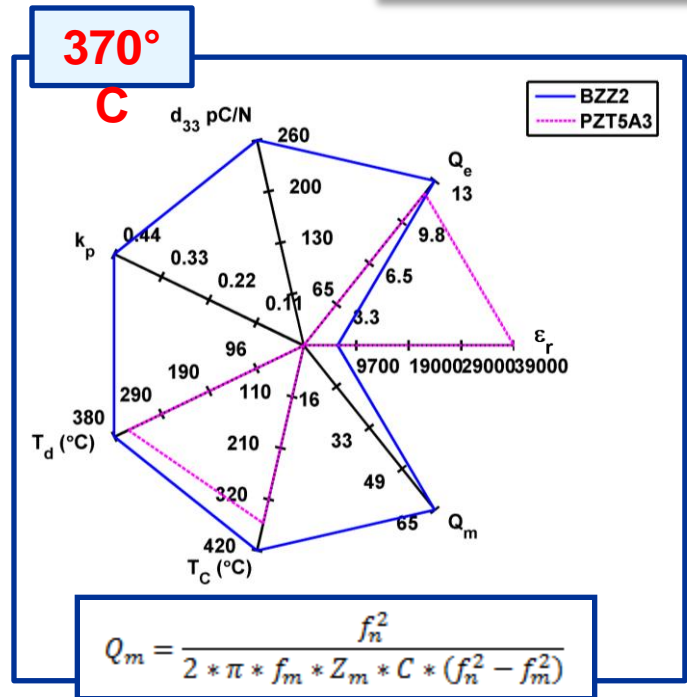
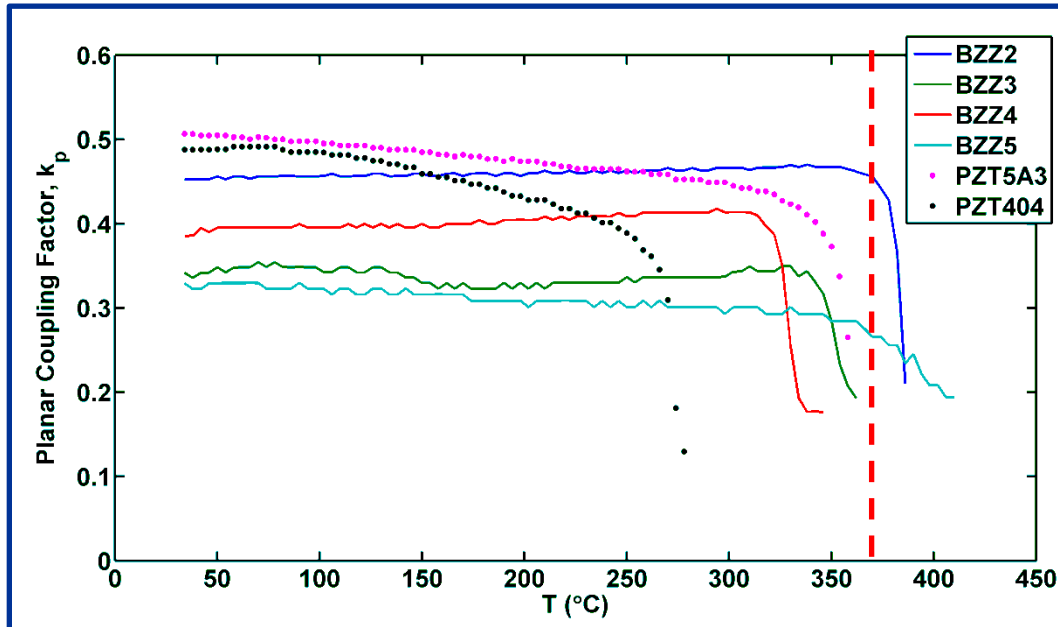
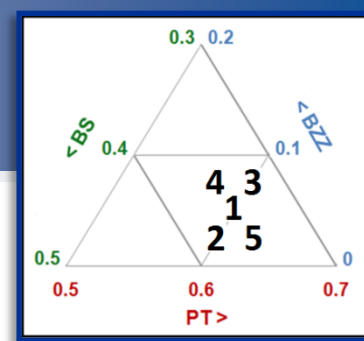
	K	$\tan \delta$	d_{33} (pm/V)*	k_p	Q_m	$T_d(^{\circ}\text{C})$	$T_c(^{\circ}\text{C})$
BZZ2	780	0.017	526	0.45	38	382	422
PZT5A3	1910	0.013	982	0.507	64	354	366



*Engineering high field d_{33} values. B. Kowalski, et al., J. Amer. Soc. Appl. Phys. 115, 084105 (2013)
 *Engineering high field d_{33} values. B. Kowalski, et al., J. Amer. Soc. Appl. Phys. 115, 084105 (2013)
 *Engineering high field d_{33} values. B. Kowalski, et al., J. Amer. Soc. Appl. Phys. 115, 084105 (2013)

BiScO₃-Bi(Zn,Zr)O₃-PbTiO₃

- PZT5A3 has depoled by 370 °C
- Q_m has increased from 35 to 65 for BZZ2, a low value for Q_m but a value equal to for PZT5A3 at room temperature.

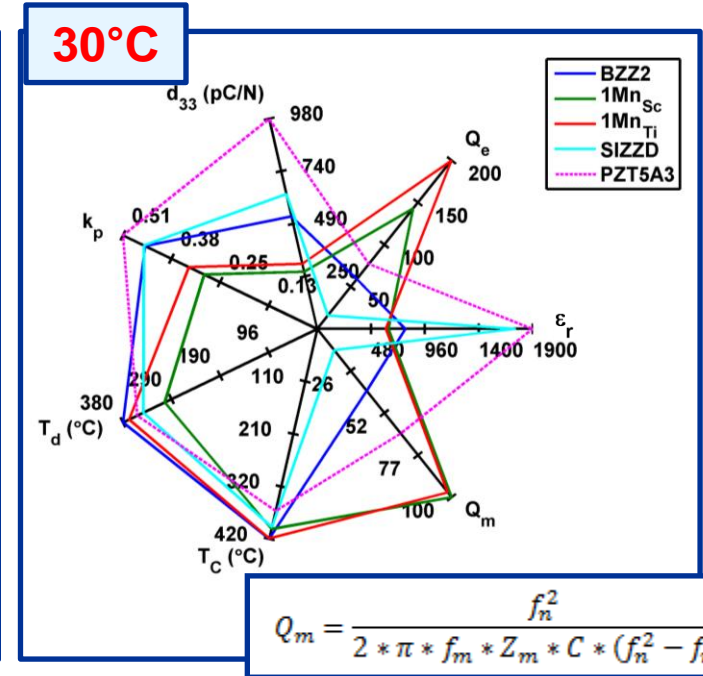
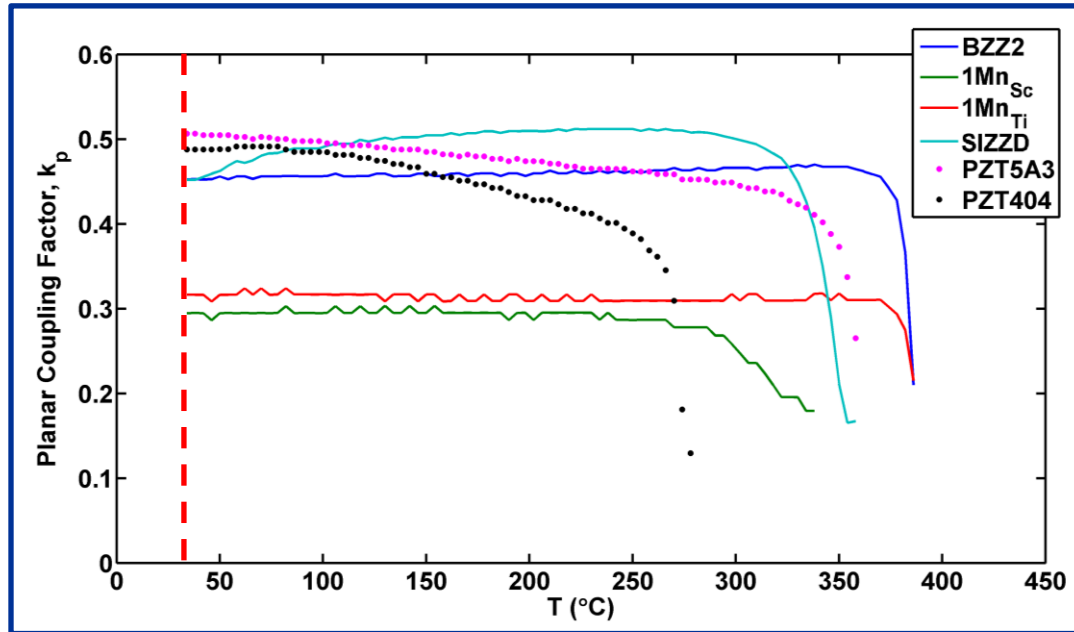


	K	tan δ	d_{33} (pm/V)*	k_p	Q_m	T_d (°C)	T_c (°C)
BZZ2	6250	0.077	260	0.44	65	382	422
PZT5A3	38670	0.08	0	0	0	354	366

* d_{33} values calculated from thickness mode

Doping of BiScO₃-Bi(Zn,Zr)O₃-PbTiO₃

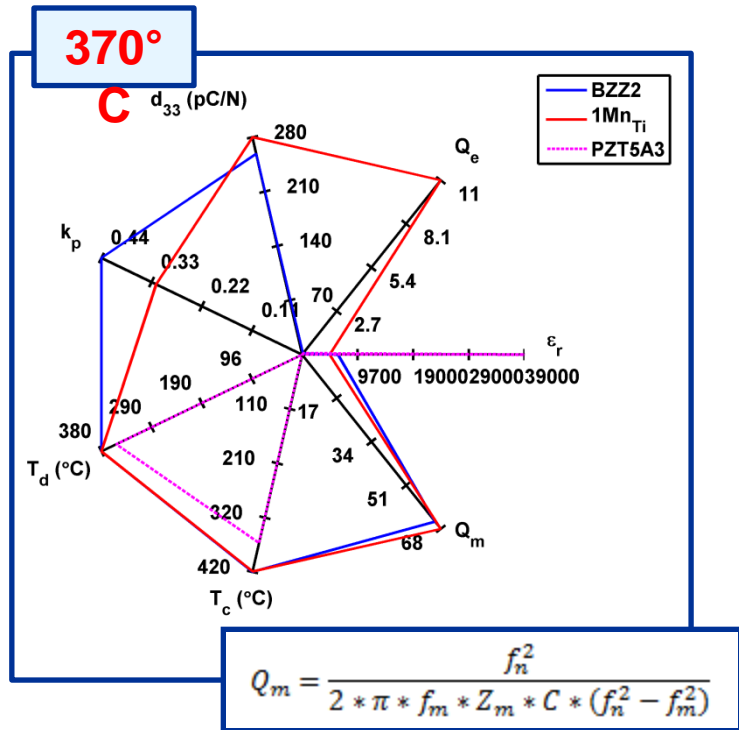
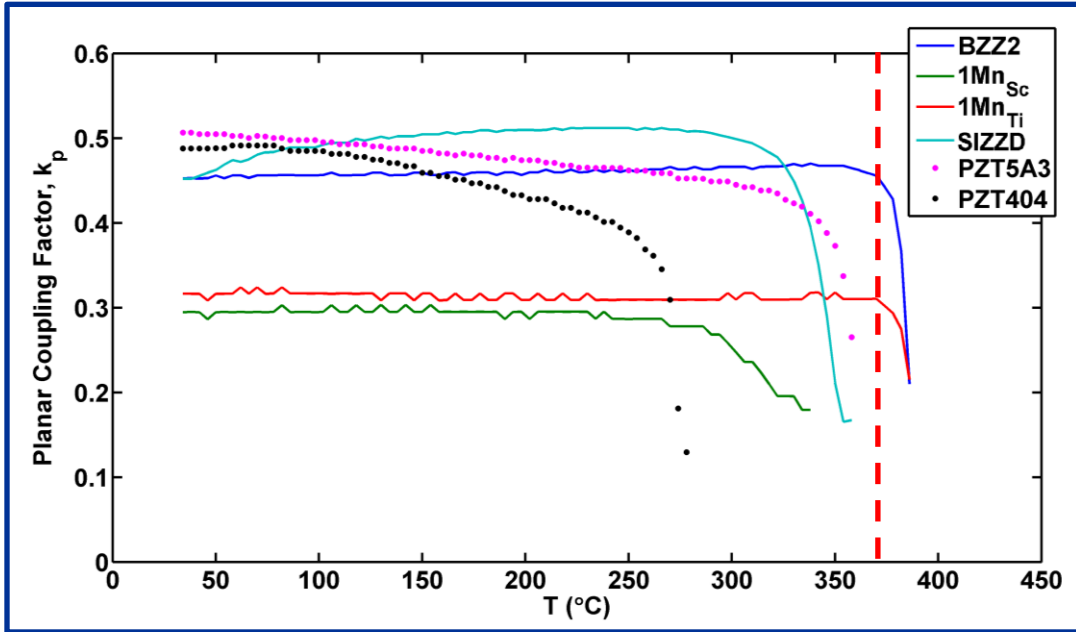
- SIZZD- BZZ1-5BI (5BZZ-30BS-5BI-60PT), BZZ2-1Mn_{Ti}



	K	tan δ	d ₃₃ (pm/V)*	k _p	Q _m	T _d (°C)	T _c (°C)
BZZ2	780	0.017	526	0.45	38	382	422
1Mn(Ti)	610	0.005	304	0.34	100	382	421
SIZZD	1760	0.062	630	0.45	13	342	398
PZT5A3	1910	0.013	982	0.507	64	354	366

*Engineering high field d₃₃ values

Doping of BiScO₃-Bi(Zn,Zr)O₃-PbTiO₃



	K	$\tan \delta$	d_{33} (pm/V)*	k_p	Q_m	T_d (°C)	T_c (°C)
BZZ2	6250	0.077	260	0.44	65	382	422
1Mn(Ti)	4828	0.09	281	0.32	68	382	421
SIZZD ⁺	6630	0.036	485	0.50	59	342	398
PZT5A3	38670	0.08	0	0	0	354	366

* Data at 300°C for SIZZD

* d_{33} values calculated from thickness mode

Summary

- Increasing demand for high temperature piezoelectrics.
- $x\text{Bi}(\text{Me}_\text{I}, \text{Me}_\text{II}, \dots)\text{O}_3 - (1-x)\text{PbTiO}_3$ solid solutions drive research.
- Factors that increase T_c (c/a ratio, FE active cations) lead to difficulties in poling, increased dielectric losses and dc conductivity.
- Depoling Temperature
- Multiple volatile cations: Complicated charge compensation possible.
- Local inhomogeneties, local random fields.
- Relearning what we have learned from PZT.
- Initial breakthrough but minor improvements since then.
- However, lots of interesting science still waiting.

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